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Selective Separation of Americium from Europium Using 2,9-Bis(triazine)-1,10-phenanthrolines in Ionic Liquids: A New Twist on an Old Story

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Bis-triazine phenanthrolines have shown great promise for f-block metal separations, attributable to their highly preorganized structure, nitrogen donors, and more enhanced covalent bonding with actinides over lanthanides. However, their limited solubility in traditional solvents remains a technological bottleneck. Herein we report our recent work using a simple 2,9-bis(triazine)-1,10-phenanthroline (Me-BTPhen) dissolved in an ionic liquid (IL), demonstrating the efficacy of IL extraction systems for the selective separation of americium from europium, achieving separation factors in excess of 7500 and selectively removing up to 99% of the americium. Characterization of the coordination environment was performed using a combination of X-ray absorption fine structure spectroscopy (XAFS) and density functional theory (DFT) calculations.

A growing global population combined with rapid development of emerging economies and a universal desire for improved standards of living drives an increasing demand for clean, renewable, and affordable sources of energy.[1, 2] Although great effort has been devoted toward the development and deployment of renewable energy sources, e.g. solar and wind power, such technologies are inherently intermittent, requiring either extensive over-building to account for day-to-day variabilities, or installation of infrastructure to store power for increased delivery during times of high demand.[3] In contrast, nuclear energy remains the only mature, carbon neutral technology capable of sustained base-load power generation. Although comprising only 15% of the global electrical power production portfolio,[4] their use in place of coal-fired power plants has nevertheless afforded dramatic environmental and public health benefits; over the past three decades, nuclear power has prevented the generation of 64 Gt CO_2-equivalent greenhouse gases and more than 1.84 million air pollution-related deaths.[4, 5]

One major criticism of nuclear power is the generation of spent nuclear fuel, for which few (if any) long-term disposal solutions are available, and the volume of which should be minimized for the sake of safety, proliferation resistance, and economics. Efficient separation of fission products and other spent fuel constituents is necessary to enable various disposal or recycle options. The minor actinides (An(III)), such as americium (Am(III)), are an example of such spent nuclear fuel constituents. A long-lifetime alpha emitter,[6] Am(III) contributes significantly to the total radiation of spent nuclear fuel, but is also a potential fuel source for next generation fuel cycles.[7] Unfortunately, the selective recovery of Am(III) is challenging due to possessing similar chemical reactivity and physical properties as lanthanides (Ln(III)). Due to their large neutron cross sectional areas, contamination with Ln(III) would prohibit the recycle of Am(III) for future nuclear power generation.

The discovery and comparatively recent development of bis(5,6-dimethyltriazine)-pyridines (Me-BTPs),[8-11] shown in Figure 1, dramatically improved the selectivity for minor actinides over other fission products. It was determined[12] that highly preorganized ligands possessing electron-donating substitutents on a rigid 1,10-phenathroline backbone greatly increased recovery of Am(III) from acidic waste media.[13-17] Unfortunately, the 2,9-bis(5,6-dimethyltriazine)-1,10-phenanthrolines (BTPhens) are insoluble in the traditional organic solvents utilized in separations processes, requiring the addition of alcohol modifiers or use of expensive fluorinated solvents.[12, 13] While more synthetically complex BTPhens have been made in an attempt to improve solubility,[12, 18] only modest improvements in performance have been achieved in common organic solvents due to the disfavored energetics of forming

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‡Electronic Supplementary Information (ESI) available: materials and synthetic methods; determination of distribution ratios, slope analysis, nitrate concentration; computational methods; X-ray absorption fine structure spectroscopy data collection and processing, principal component analysis EXAFS fitting models; Cartesian coordinates for calculated structure models. See DOI: 10.1039/x0xx00000x

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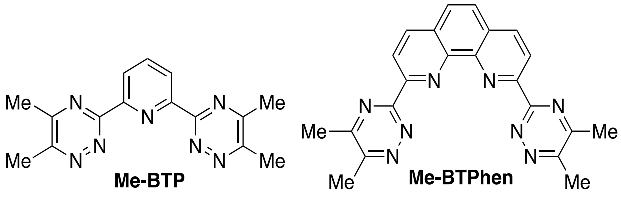

Figure 1. Structures of bis-triazine heterocycles.

highly charged metal-ligand complexes in nonpolar solvents. Preservation of charge balance either requires the undesirable co-extraction of counterions or addition of an organic-soluble cation exchanger. While BTPhen ligands display vast potential for Am(III)/Ln(III) separations, there remains tremendous need for fundamental breakthroughs in how they can be practically and efficiently deployed.

One way to alleviate the problems discussed above is to substitute ionic liquids (ILs) in place of traditional molecular solvents. ILs have a proven track record in metal ion separations[19-21] and are capable of dissolving otherwise insoluble compounds,[22, 23] can readily accommodate highly charged metal-ligand complexes, and can achieve charge balance through exchange of cationic imidazolium moieties into the aqueous phase.[24, 25] Earlier studies have reported BTPs dissolved in ILs can achieve remarkable Am(III)/Ln(III) separation factors ($SF_{Am/Eu} > 3000$),[26, 27]suggesting that if ILs could serve as a solubilizing system for BTPhens, significant improvements in separation performance could be achieved. Herein, we report the efficacy of Me-BTPhen dissolved in ILs for the separation of Am(III) from Eu(III) in nitric acid media, as well as an investigation of the resulting metal-ligand complex through application of X-ray absorption fine structure (XAFS) spectroscopy and density functional theory (DFT) calculations.

2,9-bis(5,6-dimethyl-1,2,4-triazin-3-yl)-1,10-phenanthroline (Me-BTPhen) was made following previously reported synthetic methods.[12, 13] Liquid-liquid extraction studies were done using the radioisotopes ^{241}Am(III) and $^{152/154}$Eu(III) to track and quantify the removal of each cation by the Me-BTPhen. Procedures for both synthesis and extraction experiments are provided in the Supporting Information (SI).‡

The performance of Me-BTPhen for An(III)/Ln(III) separation was investigated in three different solvents: chloroform ($CHCl_3$), trifluoromethylphenyl sulfone (known as FS-13), and the IL 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (hereafter referred to as $[C_4mim][NTf_2]$). Although Me-BTPhen dissolved into each solvent at 4 mM, when mixed with the nitric acid solution only the $[C_4mim][NTf_2]$ system was able to achieve an effective extraction of the radioisotopes. In $CHCl_3$, the Me-BTPhen would first complex then subsequently partition back into the aqueous phase. In FS-13 the ligands would complex and then precipitate at the aqueous-organic interface. The poor performance of Me-BTPhen in these molecular solvents is most likely due inability to achieve charge balance in the organic phase without extraction of three nitrate anions, and the poor solubility of the resulting highly polar metal-ligand-nitrate complex in the non-polar solvent.

When $[C_4mim][NTf_2]$ was used, the recovery of Am(III) was found to be nearly complete at ≥ 99.0 % removal at pH = 1, while the amount of Eu removed was ≤ 1.19 %. This affords a separation factor greater than 7500, which exceeds the next best separation factor reported with triazine ligand by 2.5×.[26] When the concentration of the nitric acid increased, separation factors decreased drastically due to marked suppression of the amount of Am(III) extracted, while the uptake of Eu(III) increased slightly. This result is most likely due to the increasing ionic strength of the aqueous phase which retards the cation-exchange mechanism and thus prevents charge balance in the organic solution.[28, 29] The effective distribution ratio (*D*) of Am(III) and Eu(III), corresponding separation factors (*SF*), and percent Am and Eu extracted are listed in Table 1.

$[HNO_3]$	D_{Am}	D_{Eu}	$SF_{Am/Eu}$	%Am	%Eu
0.1	94.9	0.0120	7857.1	99.0	1.19
0.5	3.25	0.132	24.6	76.47	11.67
1.0	1.07	0.152	7.0	51.57	13.21

Table 1. Distribution ratios (*D*), separation factors (*SF*), and percent recovery of Am and Eu by 4 mM Me-BTPhen for various nitric acid concentrations.

Additional experiments were performed to investigate the structure of the ligand-metal complexes formed upon extraction into $[C_4mim][NTf_2]$, in an effort to rationalize the remarkably high efficiency for Am removal. Slope analysis was applied to determine the stoichiometry of ligand-metal complex. The ligation of the metal species can be determined from the slope of the line in the plots, revealing the Me-BTPhen forms a 2-to-1 complex (Figure S3), as reported previously in the literature.[27, 30] While clearly demonstrating the number of ligands bound to each metal, there remained uncertainty as to whether the IL solvent could also be participating in the extraction through direct interaction with the metal cation in the inner coordination sphere. In an effort to determine the complete structure of the complex in solution, we applied high level DFT calculations complemented by XAFS spectroscopy.

Eu(III) was chosen as an Am(III) surrogate for XAFS investigations due to possessing similar size and chemical reactivity while not presenting a radiological concern. DFT calculations were performed on both Eu(III) and Am(III) complexes with Me-BTPhen using the Gaussian 09.[31] The potential Eu(III) and Am(III) complexes investigated consisted of 2 Me-BTPhen molecules and NO_3^-, NTf_2^-, H_2O, OH^-, or no anion in the first coordination shell of the metal ion. A figure displaying the geometrically optimized structures of the corresponding complexes with Eu(III) is given in Figure 2.

The coordination environment of the Eu-Me-BTPhen complex in $[C_4mim][NTf_2]$ was also investigated through XAFS spectroscopy. XAFS data were collected at the Eu L(III)-edge (6977 eV) on beamline 11-2 at Stanford Synchrotron Radiation Lightsource, Data were processed and analyzed using open source fitting software.[32-34] Further details regarding data collection and processing are provided in the SI.

Principal component analysis of the nine normalized

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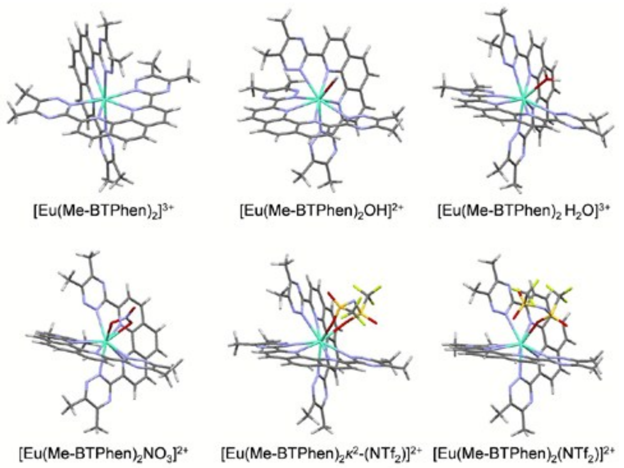

Figure 2. Geometry optimized Eu-Me-BTPhen complexes obtained from DFT calculations. The name of the complex is provided below the corresponding structure. Eu is turquoise, C grey, O red, S yellow, and H white.

absorption datasets resulted in identification of only one mathematical component at the > 99.9% confidence level (Figure S4). This statistical approach suggests there is only one solution component contributing to the spectral response. DFT-optimized complexes (Figure 2) were used to prepare structure models for fitting to the EXAFS data. Reasonable preliminary fits were obtained for $[Eu(Me\text{-}BTPhen)_2]^{3+}$, $[Eu(Me\text{-}BTPhen)_2(H_2O)]^{3+}$, $[Eu(Me\text{-}BTPhen)_2(NO_3)]^{2+}$, and monodentate $[Eu(Me\text{-}BTPhen)_2(NTf_2)]^{2+}$. Similar to EXAFS spectra collected on $[Eu(CyMeBTPhen)_2(H_2O)](NO_3)_3$ crystals or the solvated compound in cyclohexanone,[27] a shoulder is apparent at 1.5 Å in the Fourier transformed data, albeit more pronounced for the IL spectrum, and best resolved by inclusion of a tightly coordinating water molecule. Similar spectral contributions cannot be reasonably achieved with a chelating NO_3^- due to bond length considerations (Figure S8). This is further supported by a constant NO_3^- concentration post-extraction, also indicating charge balance is achieved by exchange of 3 cationic $[C_4mim]^+$ per Eu^{3+} rather than extraction of a $Eu(NO_3)_3$ complex. While the spectroscopic feature could be resolved with a monodentate-bound NTf_2^-, the sterics of this putatively coordinating ligand are unlikely to accommodate the short interatomic distance necessary. Importantly, a deprotonated $[Eu(Me\text{-}BTPhen)(OH)]^{2+}$ model system also failed to provide an adequate fit of the data due to the commensurate lengthening of the first shell bond lengths for the Me-BTPhen ligand (Figure S9). The aforementioned discarded fits are displayed in the SI, accompanied by their corresponding DFT-based model (Figures S7-S10).

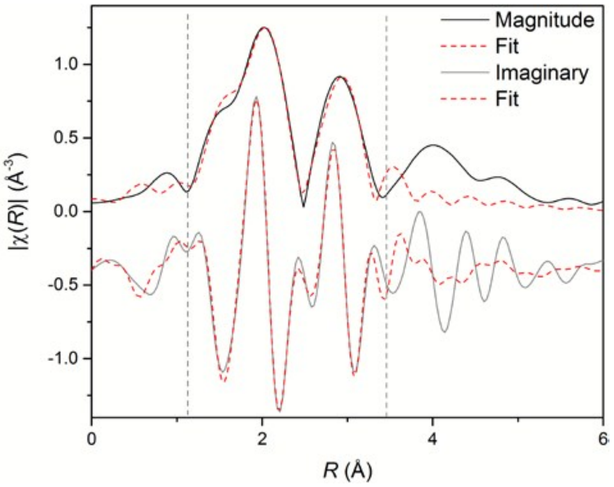

Figure 3 Fourier transform of the Eu L_{III}-edge EXAFS spectrum in *R*-space (black line), with accompanying fit afforded by the $[Eu(BTPhen)_2(H_2O)]^{3+}$ model. The imaginary component (grey line) and fit are offset beneath. Grey dashed lines denote the fit window.

In contrast to complexes displaying inner sphere interactions between Eu and an anion, the comparatively simple 1:2 $[Eu(Me\text{-}BTPhen)_2(H_2O)]^{3+}$ complex afforded a good fit of the EXAFS data in both first and second coordination spheres (Figure 3), as well as with regards to reasonable fitting parameters (Table 2). Efforts were made to improve the goodness of fit through inclusion of more multiple scattering paths, as well as through addition of a separate σ^2 for the tightly coordinating H_2O. However, application of the F-test revealed the apparent gains were not statistically significant.[35-37] Expansion of the data range and inclusion of distant scatterers was also attempted in an effort to fit the feature at 4 Å, but was ultimately unsuccessful. The possibility of a dimeric complex was also considered by investigating a model generated from a crystal structure containing $Eu_2Phen_2(OH)_2$, but the Eu-Eu scattering path did not align well with the feature at 4 Å and had a deleterious effect. It is expected multiple scattering paths and scattering from distant atoms on Me-BTPhen ligands are convoluted with those from anions in the second coordination sphere, making definitive refinement of these features particularly challenging.

Path	Coord. No.	Bond Length (Å)	σ^2 ($\times 10^{-3}$ Å^2)
$Eu \rightarrow OH_2$	1	1.93 ± 0.02	4.9 ± 0.09
$Eu \rightarrow N_{phen}$	4	2.53 ± 0.02	4.9 ± 0.09
$Eu \rightarrow N_{azine(1)}$	4	2.55 ± 0.01	4.9 ± 0.09
$Eu \rightarrow C_{phen}$	4	3.39 ± 0.02	2 ± 0.1
$Eu \rightarrow N_{azine(2)}$	4	3.43 ± 0.01	2 ± 0.1
$Eu \rightarrow C_{azine}$	8	3.44 ± 0.01	2 ± 0.1
$Eu \rightarrow N_{phen} \rightarrow C_{phen}$	24	3.64 ± 0.02	7 ± 0.1
$E_0 = 9.5 \pm 0.8$		R = 0.96%	$\chi_\nu^2 = 32.7$

Table 2. Data for EXAFS fit with $[Eu(Me\text{-}BTPhen)_2(H_2O)]^{3+}$ Structure Model.

Based on the structural information obtained from DFT and EXAFS, we can speculate on the possible origin of enhanced Am(III) over Eu(III) selectivity in the IL solvent compared to traditional organic solvents. As nitrate anions are extracted together with the trivalent metal ions into the organic phase, present DFT calculations and crystallographic evidence[27] suggest that one nitrate can enter the inner sphere of the complex and adopt a chelate coordination mode. Substitution of bidentate nitrate in organic solvent by H_2O in $[C_4mim][NTf_2]$ leads to a shorter average metal ion-ligand bond distance and a stronger ligand binding (Table S1), which could in turn lead to a higher selectivity for Am(III) over Eu(III).

Conclusions

In conclusion, we report the remarkable capability of a simple Me-BTPhen extractant to achieve highly efficient partitioning of Am(III) from Eu(III) upon dissolution in commercially available [C_4mim][NTf_2]. Effecting separation factors in excess of 7500, this constitutes the most efficient system reported to date for a single-strike separation, exceeding the previous best soft *N*-donor system by more than 2.5× and the current state-of-the-art organic system by 41×. Complementary characterization approaches including slope analysis, DFT calculations, and XAFS confirmed the formation of a 2:1 complex upon extraction into the IL phase, while fitting of the EXAFS spectrum confirmed a coordination number of 9 and supports the non-interaction of the anion in the first coordination sphere. Implementation of this technology in the processing of spent nuclear fuel could result in tremendous cost savings from reduction in facility footprint, diminished quantities of solvent, smaller volumes of final waste streams requiring long-term storage.

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Keywords: selectivity • lanthanides • size-based separation • DFT • solvation effects • XAFS

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